labeled irumamycin exhibited additional satellites for all carbon signals each of which appeared as a doublet. These satellite peaks suggested that two intact $^{13}CH_3{}^{13}COOH$ units were incorporated at adjacent sites. Measurement of intra- and intermolecular $^{13}C$–$^{13}C$ coupling constants of acetate unit permitted derivation of partial structures II and III. The feeding experiment using [1-$^{13}C$]propionate indicated very strong enrichment for eight carbon signals at $\delta$ 211.5 (C-25), 134.6 (C-15), 117.2 (C-5), 81.9 (C-19), 80.3 (C-7), 77.8 (C-17), 66.4 (C-23), and 36.1 (C-21). Examination of the $^{13}C$–$^{13}C$-coupled signals arising from the incorporation of [1,2-$^{13}C$1propionate established partial structures IV and V. The biosynthetic evidence for structures IV and V is in harmony with the structures of **5** and with the two olefinic segments proposed on the basis of 400-MHz $^1H$ NMR spectral analysis of **1**, respectively. The presence of the $\alpha,\beta$-epoxy $\alpha',\beta'$-ethyl ketone moiety in **1** was also supported by the long-range $^{13}C$–$^{13}C$ coupling ($^3J_{CC}$ = 11.3 Hz) between the epoxy carbon (C-24, $\delta_C$ 64.6) and the methylene carbon of ethyl ketone (C-26, $\delta_C$ 28.9) because of high incorporation of propionate. It is noteworthy that both epoxide carbons ($\delta_C$ 66.4 and 64.6, $J_{CC}$ = 28.1 Hz) arise from one propionate molecule. Combination of structure I derived from chemical degradation with segments II, III, IV, and V deduced from biosynthetic studies leads to the 20-membered macrolide structure **1** containing a six-membered ring hemiketal for irumamycin.

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**Registry No.** **1**, 81604-73-1; **2**, 83845-28-7; **3**, 21630-96-6; **4**, 36051-78-2; **5**, 83861-68-1; **6**, 83845-29-8; **7**, 83845-30-1.

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## Generation of Trialkylcyclopropenyl Radicals by Pulse Radiolysis and Radical–Ion Complex Formation[1]

*Summary:* Trimethylcyclopropenyl radical, generated by pulse radiolysis from the corresponding cation, complexes with the cation.

*Sir:* In spite of their theoretical interest, cyclopropenyl radicals have not been extensively characterized by physical methods, and their chemistry has been little explored. This can be attributed to the difficulty encountered in their preparation and to their high reactivity rendering them short-lived except in matrix isolation.[2] An obvious way to prepare a cyclopropenyl radical is to add an electron to the aromatic cation as has been done in the electrochemical reduction of several cyclopropenium ions.[3]

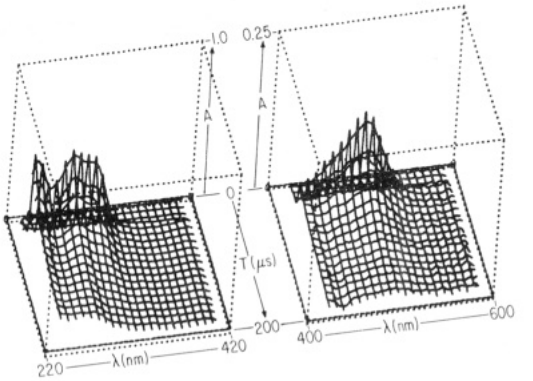


**Figure 1.** Time dependent UV and visible spectra of pulse-radiolyzed, He-saturated, aqueous solutions containing 0.001 M $Cy^+$ and 0.01 M *tert*-butyl alcohol. At 303 nm $\epsilon$ = 6600, and at 500 nm $\epsilon$ = 2800.

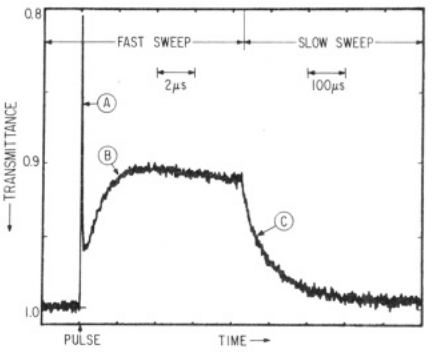


**Figure 2.** Photomultiplier response vs. time of a pulse-radiolyzed, He-saturated, aqueous solution of 0.001 M $Cy^+$ and 0.1 M *tert*-butyl alcohol (ionic strength = 0.1, pH 5.1, 25 °C, 500 nm, 10-ns pulse width): A, formation and disappearance of the hydrated electron; B, formation of $Cy^{2+}$; C, decay of $Cy_2{}^+$.

Unfortunately, the electrochemical method is not very suitable for making spectroscopic observations on the highly reactive radical produced on the electrode surface. We report here the formation of trimethylcyclopropenium radical in homogeneous solution via pulse radiolysis from the trimethylcyclopropenium cation.[4] Unexpectedly, a remarkable complex formation between the radical and the cation was found to occur.

When an aqueous solution of trimethylcyclopropenyl fluoroborate, containing 0.1 M *tert*-butyl alcohol as an OH scavenger, was subjected to a submicrosecond pulse from the ANL 20-MeV Linac, a transient absorption spectrum was recorded on a streak camera system.[5] The spectrum and its time evolution are shown in Figure 1. By measuring the rate of disappearance of the hydrated electron at 600 nm and the rate of appearance of the transient peak at 500 nm it became apparent that the carrier of the spectrum is not the primary reduction product of the ion. This is graphically shown (Figure 2) in the photomultiplier output measured at 500 nm where the sharp spike corresponds to the production and disappearance of the hydrated electron. The two rates are sufficiently different that it was possible to separate them and measure the apparent rate constant for the buildup of the 500-nm absorption, which was identical with the buildup of the absorption in the 300-nm region. By varying the concentration of the cation and by changing the radiolysis dose, it was shown that the formation of the carrier of the

(1) Work performed under contract with the Offices of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, Contract No. W-31-109-ENG-38.
(2) Closs, G. L.; Evanochko, T.; Norris, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 350.
(3) Wasielewski, M. R.; Breslow, R. *J. Am. Chem. Soc.* **1976**, *98*, 4222.
(4) Closs, G. L.; Böll, W. A.; Heyn, H.; Dev, V. *J. Am. Chem. Soc.* **1968**, *90*, 173.
(5) Schmidt, K. H.; Gordon, S.; Mulac, W. A. *Rev. Sci. Instrum.* **1976**, *47*, 356.

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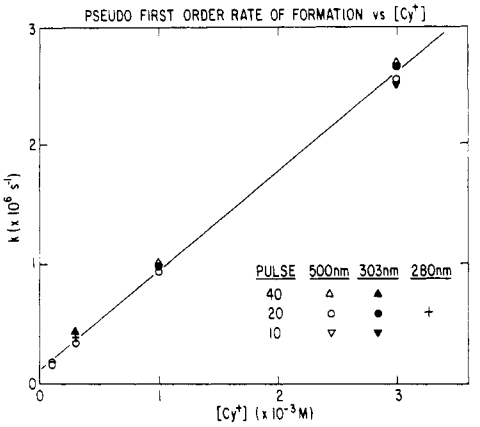


**Figure 3.** Pseudo-first-order rates of formation of $Cy_2^+$ vs. $[Cy_+]$ at different wavelengths and pulse widths (in nanoseconds).

spectrum is first order in the cation and first order in the primary reduction product. On the basis of these kinetics, we can write eq 1 and 2, where $Cy^+$ is the trimethyl-

$$Cy^+ + e^-_{aq} \xrightarrow{k_1} Cy\cdot \quad (1)$$

$$Cy\cdot + Cy^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Cy_2^+ \quad (2)$$

cyclopropenium cation and Cy· is the cyclopropenyl radical. The rate of electron capture at 25 °C is diffusion controlled; $k_1 = 3.2 \times 10^{10}$ $M^{-1}$ $s^{-1}$ (at zero ionic strength). The reversibility of reaction 2 is clearly established from the concentration study, and the values of $k_2 = 8.3 \times 10^8$ $M^{-1}$ $s^{-1}$ and $k_{-2} \approx 3 \times 10^5$ $s^{-1}$ are taken from the slope and intercept of a plot of the apparent rate constant of formation of $Cy_2^+$ vs. $[Cy_+]$ (Figure 3). This equilibrium corresponds to $\Delta G = -4.7$ kcal/mol for the formation of the complex.

The rate of disappearance of $Cy_2^+$ is mostly second order with some small first-order component. A high concentration of $Cy^+$ retards the rate, indicating that the $Cy_2^+$ disappears via dissociation (eq 3–6). The major product

$$Cy_2^+ \rightleftarrows Cy^+ + Cy\cdot \quad (3)$$

$$Cy\cdot + Cy\cdot \rightarrow HMB \quad (4)$$

$$Cy\cdot + Cy_2^+ \rightarrow HMB + Cy^+ \quad (5)$$

$$Cy\cdot + R\cdot \rightarrow Cy\text{-}R \quad (6)$$

is hexamethylbenzene (HMB, ~70%) which can be formed either via reaction 4 or 5. Reaction 6 in which R· is the *tert*-butyl alcohol radical is probably responsible for the less than quantitative yield of HMB. At present the mechanism for the formation of HMB is unclear.

At this point there is no information on the structure of the complex, although we believe a sandwich structure to be the most likely. The band at 500 nm is probably a charge-transfer transition promoting the odd electron from one ring to the other.

This complex differs from other known cation dimers of aromatic hydrocarbons[6] in which the electron-deficient half of the dimer is nonaromatic, while in the complex described here the aromatic component functions as the electron acceptor.

The spectrum of Cy· could be deduced from absorption measurements taken at very short times after the electron pulse although it was not obtained completely free of $Cy2^+$. A cleaner spectrum (Figure 4) was obtained in the pulse

(6) Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1970**, *66*, 2939.

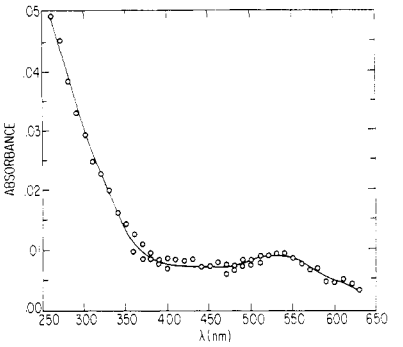


**Figure 4.** Composite transient spectrum produced by pulse radiolyzing a He-saturated solution of 0.001 M tri-*tert*-butylcyclopropenyl perchlorate (0.1 M *tert*-butyl alcohol; $[e^-_{aq}]_0 \approx 10^{-5}$ M.

radiolysis of tri-*tert*-butylcyclopropenium perchlorate. In this case, there is no evidence for complexation of the radical and the cation, presumably due to steric hindrance. The lifetime of this radical is substantially longer than that of the trimethyl derivative, and it disappears with mixed-order kinetics. The low extinction coefficient ($\epsilon \sim 200$ at 500 nm) and the steadily rising structureless feature of the spectrum suggests a substantial geometry change between ground and excited states.[7]

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**Registry No.** Trimethylcyclopropenyl radical, 60528-77-0; trimethylcyclopropenyl cation, 26827-04-3; tri-*tert*-butylcyclopropenyl radical, 60528-80-5; tri-*tert*-butylcyclopropenyl perchlorate, 19985-80-9.

(7) After this manuscript had been submitted, another contribution on trimethyl cyclopropenyl radicals appeared: Sutcliffe, R.; Lindsay, D. A.; Griller, D.; Walton, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1982**, *104*, 4674.

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## Enzyme-Catalyzed Synthesis of *N*-Acetyllactosamine with in Situ Regeneration of Uridine 5′-Diphosphate Glucose and Uridine 5′-Diphosphate Galactose

*Summary:* *N*-Acetyllactosamine has been synthesized on 80-mmol scale by an enzyme-catalyzed procedure starting from glucose 6-phosphate, *N*-acetylglucosamine, and phosphoenolpyruvate in a route requiring in situ (re)generation of UDP-galactose (Scheme I). UDP-galactose was generated from UDP-glucose by UDP-galactose epimerase catalyzed epimerization of UDP-glucose, which was in turn generated from UTP and glucose 6-phosphate with catalysis by phosphoglucomutase and UDP-glucose pyrophosphorylase. Pyrophosphatase was used to catalyze the hydrolysis of the inorganic pyrophosphate released to drive the reaction. UTP was regenerated from UDP and phosphoenolpyruvate with catalysis by pyruvate kinase.

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(2) NSF Predoctoral Fellow.

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